Simulation of a Solvate Ionic Liquid at a Polarisable Electrode with a Constant Potential

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Abstract

Solvate ionic liquids have the potential for use in a wide range of electrochemical devices. The interfacial nanostructure of these liquids largely determines the performance of such applications. Here we discuss the nanostructure and calculated the capacitance of a solvate ionic liquid–electrode interfaces, where the electrode has a constant potential, and is thus inherently polarisable. Lithium ions from the lithium glyme solvate ionic liquid are found within 0.5 nm of the electrode at all voltages studied, however, their solvation environment varies with voltage. Our study provides molecular insight into the electrode interface of solvate ionic liquids, with many features similar to pure ionic liquids. A comparison with previous studies of the same electrolyte using the fixed surface charge boundary condition is also illuminating, informing future computational studies of electrolyte–electrode interfaces.

Introduction

Solvate ionic liquids are a new class of ionic liquids formed of a salt, usually a lithium salt, and a chelating solvent molecule. If the chelation is of significant longevity and prevalence, then a liquid comprised solely of ions like a conventional ionic liquid is formed.¹ Solvate ionic liquids are relevant to a range of applications, most prominent is their possible usage as electrolytes for lithium sulphur batteries.²³ One such ionic liquid is lithium bistriflimide tetraglyme – Li(G4)TFSI. Tetraglyme (G4) is a chelating solvent from the glyme homologous series sketched in Fig. 1A. Li(G4)TFSI is formed by dissolution of lithium bistriflimide in tetraglyme (Fig. 1B). In these liquids, such a large proportion of lithium ions are chelated to glyme molecules that the solution exists as liquid comprised almost solely of ions like a conventional ionic liquid.¹

In our previous work, we simulated the nanostructure of Li(G4)TFSI at electrodes using the constant surface charge method.⁴ The observed nanostructure was unusual, with little direct coordination of lithium cations to the electrode. However, it did not fully match the interfacial structure observed in atomic force microscopy experiments.⁵ This work aims to unify the results of experiments and simulations, by performing molecular dynamics simulations using a fixed potential electrode method.

Methods

The simulations are performed using the constant potential method implemented by Wang et al.⁶ based on previous work by Reed et al.,⁷ Gingrich et al.,⁸ and Siepmann et al.⁹ This
implementation operates through the use of the LAMMPS molecular dynamics software.\textsuperscript{10} Similar methods were previously used in several simulations of ionic liquids\textsuperscript{11,12} as well as of lithium-based electrolytes.\textsuperscript{13}

Force fields used for the ionic liquid were developed by Shimizu et al.,\textsuperscript{14} and are the same as used in our previous study.\textsuperscript{4} These force fields are based on the OPLS-AA force field\textsuperscript{15} with the CL&P parameters used for bistrifflimide,\textsuperscript{16} and the Åqvist force field used for lithium cations.\textsuperscript{17} As in the previous studies, ion charges are scaled to obtain accurate transport properties. For unlike pairs the standard OPLS-AA combination rules are used.\textsuperscript{15}

The simulation box has a length of 10 nm in the z-direction. It consists of two electrodes – three-layered graphene sheets with the inter-layer separation of 0.335 nm and separated by 8.000 nm from one other. The lateral dimensions of each sheet are set as 4.673 nm by 4.331 nm, the same as the box dimensions in x- and y-directions. An implicit vacuum slab of 20 nm is placed between the two ends of the box. Electrostatic forces acting on the particles within the system are calculated by means of the particle–particle particle-mesh (PPPM) solver and the Ewald summation.\textsuperscript{18–20} For the force calculation step, the Coulomb and van der Waals cutoffs in this system are set to 1.4 nm, and the PPPM accuracy set so that forces are calculated with a maximum relative error of $1 \times 10^{-6}$.

The fixed potential method works by fixing the electric potential ($\Psi_i$) on each electrode so that it is equal to external potential ($V$). This equation can be solved for each atom by 3D Ewald summation incorporating the Yeh–Berkowitz slab correction.\textsuperscript{21} To render the Ewald sum, non-conditionally convergent the electrode atoms are modelled as Gaussian distributions of charge with a characteristic width $\eta$. For this work, a relationship of, $\eta^{-1} = 19.79 \text{nm}^{-1}$, as used as in previous works.\textsuperscript{6,7}

In the simulations presented here, the 8 nm by 4.673 nm by 4.331 nm gap between the electrodes is packed to bulk density with 346 ion pairs and glyme molecules. The initial configurations are generated with the packmol algorithm\textsuperscript{22} followed by steepest descent energy minimisation. The temperature of the system is set to 300 K with atom velocities set to replicate the Boltzmann distribution; the temperature is raised from 300 K to 500 K over the course of 1 ns. At this point, the constant potential boundary condition is applied to the electrodes. Equal and opposite external potentials are applied to the two electrodes allowing for us to simulated boxes with potential differences between electrodes ($\Delta \Psi$) of 0 V to 4 V. The system is then cooled from 500 K to 300 K over the course of 1 ns. A run is then performed at 300 K for 7 ns with the first 3 ns treated as an equilibration run and the subsequent 4 ns treated as the production run. This process is repeated for four replicas at each voltage. The Nosé–Hoover thermostat is used throughout the simulations.\textsuperscript{23,24}

Results and Discussion:

Fig. 2 shows the interfacial density of three components for $\Delta \Psi = 0,1,2,3,$ and 4 V. To get a better idea of the form of coordination shells, the following guide atoms are used for each

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure1.png}
\caption{Panel A: a scheme showing the general formula of a glyme polymer or oligomer. Panel B: the mixing of lithium bistriflimide Li[TFSI] with tetraglyme G4 to form the solvate ionic liquid Li(G4)TFSI.}
\end{figure}
molecule: glyme oxygen atom density shown in red, bistriflimide nitrogen atoms shown in blue, and lithium cations shown in purple. As is observed for all liquids at a solid interface the presence of the surface leads to the formation of an ordered structure.

Firstly, for every external potential lithium cations are present in the first layer of the structure.

Secondly, a multilayer structure is observed at large positive and negative external potentials. For negative external potentials in Fig. 2, an area of cationic excess can be observed at a distance of 1.1 nm, and an area of net anionic density at a distance of 1.4 nm. Features which are symptomatic of the overscreening multilayer structure of conventional ionic liquids. The same features are seen at positive electrodes where the anionic excess can be observed at a distance of 0.8 nm and the cationic excess at distances of roughly 1.2 nm. Which, is again symptomatic of an overscreening multilayer structure. These areas of net excess take place at different relative locations due to the different thickness of the first interfacial layer, with the first interfacial layer of negative external potentials being considerably thicker.

Thirdly, within the first interfacial layer there appear to be two lithium peaks – the first at 0.3 nm and a second at 0.4 nm. An additional peak follows these peaks at about 0.55 nm, which sees its density rise with increasingly negative surface charge. The size of peaks at 0.3 nm and 0.4 nm has a more complicated dependence on the external potential. The peak at 0.3 nm is representative of lithium cations in closest possible contact with the electrode, and the peak at 0.4 nm is due to ions which have some coordinating ligands on the electrode side of their coordination shell. At the negative electrode the peak at 0.3 nm increases in size relative to the peak at 0.4 nm with increasingly negative potential difference, indicating that with increasingly negative electrode potential the lithium cations move closer to the surface to screen the surface charge.

The coordination environments of the lithium ions in the first interfacial layer, within 0.5 nm of the electrode, are captured by the simula-

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**Figure 2**: Plots showing the interfacial number density of the components of solvate ionic liquids. The structural formula of bistriflimide anion and lithium–glyme complex cation are shown on the top. Coloured atoms indicate the colour code in the plot. These plots show densities through the whole simulation cell for simulations run with potential differences between electrodes. The negative electrode sits on the left of the graph, while the positive electrode sits on the right of the plot.
Figure 3: Panel A: Snapshots of the lithium ions and the oxygen atoms in their coordination shells within 0.55 nm of the negative electrode for $\Delta\Psi = 4$ V, 2 V, and 0 V. Lithium cations are shown in orange, bistriflimide oxygens are shown in blue, and glyme oxygens are shown in violet. Panel B: Distribution of charge in the inner layer of atoms in the electrode. Plots are shown for potential differences of 4 V (in blue for the negative electrode and red for the positive one), 2 V (in cyan for the negative electrode and magenta for the positive electrode), 0 V (green).

As the electrode can be polarised depending on its local environment, the area nearest to the extend stings of lithium bistriflimide complexes take on a more positive surface charge, as can be seen in Fig. 3), and those areas of the electrode closest to the lithium glyme clusters will take on a more negative surface charge.

Finally, we move to a discussion of the capacitance. As fluctuations in charge on the electrode are related to correlations with liquid species in the near vicinity. The differential capacitance can be extracted from the oscillations in electrode charge within time by using the relationship,

$$ C(\Delta\Psi) = \frac{\partial Q}{\partial \Delta \Psi} = \frac{\langle \delta Q^2 \rangle}{k_B T} \quad (1) $$

where $C(\Delta\Psi)$ is the potential dependent capacitance, $\Delta\Psi$ is the external potential difference, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\delta Q$ is defined as,

$$ \delta Q = Q - \langle Q \rangle, \quad (2) $$
where $Q$ is the charge of the whole electrode. $C(\Delta \Psi)$ is the total capacitance of the simulated two-electrode system.\textsuperscript{28} Usually, in theory and computations, a one-electrode capacitance is plotted against the potential drop from the electrode to the bulk-like region.\textsuperscript{29} On such a plot the curve might have a single-hump or a double-hump shape. Herewith, both constant surface charge and constant potential methods provide the data for plotting such capacitance–potential drop,\textsuperscript{30} yet only the latter one allows for straightforward calculation of $C(\Delta \Psi)$. Fig. 4 shows the resulting total capacitance curve on the $\Delta \Psi$-scale. The curve has a maximum at roughly 2V, which is equivalent to the double-hump shape on the potential drop scale. A similar plot for a conventional ionic liquid was presented in Ref.\textsuperscript{26} Thus, the behaviour is symptomatic of an ionic liquid nanostructure, and together with the simulated nanostructure suggests that solvate ionic liquids behave in a manner similar to conventional ionic liquids\textsuperscript{31,32} and their solutions with lithium salts.\textsuperscript{33,34} It should be noted that this capacitance curve does not reflect what would be seen for the diluted solution of lithium salt in an organic solvent. It will be interesting to see how this curve and capacitance, in general, would evolve with time particularly when compared to conventional ionic liquid solutions.

In a somewhat related point. Due to the box size and simulations length, it has not been possible, as usual with simulations of this type to extract screening lengths from these simulations. However, recent work has suggested the change in screening length with increasing dilution of these liquids would be a highly interesting quantity.

The results in this study differ significantly from previous studies.\textsuperscript{4} Primarily in the presence of a dechelation dynamic, which is induced by surface polarisability. Moreover, the nanostructure in this study does agree with previously obtained atomic force microscopy results.\textsuperscript{5} This study raises a question about the veracity of using simple fixed charge simulations for systems featuring ions and coordinating solvents, to understand interfacial behaviour at electrodes. The heterogeneous surface charge distribution clearly affects the solvation of lithium ions by the glyme at the interface. A more profound effect than observed for the interfacial structure in conventional ionic liquids.\textsuperscript{28,30} Moreover, fixed charge simulations do still provide strong indications of how a liquid would behave at a charge dielectric surface, where the surface charge is equally distributed among the atoms of the same type. Which can inform the results obtained from experiments performed on these types of surfaces, such as surface force or electrowetting experiments.\textsuperscript{35–38}

The coordination behaviour observed in this paper have wide-reaching implications for the implementation of solvate ionic liquids in technology. The presence of dechelation dynamics is likely to have a large role in both charge transfer and wear of electrodes. The level to which this needs to be maximised and minimised is not apparent from this study. However, it is likely that it will be possible to control for this while maintaining the bulk solvate ionic liquid type behaviour as any change to allow for easier dechelation at the electrode can be counteracted in the bulk by using an even less readily coordinating ion.\textsuperscript{1,39}

It is enticing to think that the behaviours observed here may be the reason for a previous result by Moon \textit{et al.}\textsuperscript{40} where concentrated solutions of lithium bistriflimide in tetraglyme exfoliate graphitic minerals, but solvate ionic liq-
uids do not. This alongside an interest in seeing the effect of dilution on the capacitance curve, alongside the anomalous screening lengths observed experimentally for diluted lithium glyme solutions,\textsuperscript{41} provides a motivation for future simulations of diluted solvate ionic liquids at fixed potential electrodes.

**Conclusion**

This study has shown that solvate ionic liquids adopt a multilayer type interfacial structure at fixed electrode potential, a behaviour similar to that observed for conventional ionic liquid. This structure is very different from the structure observed in past studies when a fixed surface charge was applied to the electrodes instead.\textsuperscript{4}

The coordination environment of lithium cations in the first interfacial layer was seen to be vastly different for the coordination environment in the bulk with a far larger number of lithium cations coordinated to bistriflimide anions. This difference will affect charge transfer at electrodes but may also explain the differences in the intercalation of lithium ions into graphitic electrodes.\textsuperscript{40}

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**References**


